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An experimental investigation of X-ray excitation states in solids

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With 13 figures in the text

ABSTRACT

When X-ray lines are recorded, the energy of the bombarding electrons is generally high above the excitation potential. In the present work recordings have been made with the energy of the electrons only a few electron volts above the threshold value. By comparing the spectral position of such a line with the position of an ordinarily recorded one, a small wavelength shift has been observed. The shift is discussed with reference to a recently reported theory of X-ray excitation states in solids. Determinations have been made for the $K\alpha_1$ line of metallic Cr and its oxide Cr_2O_3. A difference in the K excitation potential between metal and oxide (chemical shift) is also reported.

I. Introduction

In 1939 Landshoff [1] attempted to explain the edge structure in X-ray spectra by considering transitions into a series of discrete states. In calculating the energy of these states he used a model in which the excited electron was bound close to the positive parent ion. In connection with the interpretation of the experimental evidence for a pronounced maximum in the absorption near the edge (white line) Cauchois and Mott [2] in 1949 made a similar assumption and explained the edge structure as due to the formation of exciton levels. In 1951 Friedel [3] made a theoretical investigation of the distribution of electrons around a positive impurity in monovalent metals. He applied the results on X-ray spectra treating the electron vacancy in one of the inner shells as a positive impurity.

A development of the fundamental excitation aspects to a general theory for the solid state and with proper respect to X-ray spectroscopy has recently been given by Parratt [4]. Some essentially new features have also been introduced, the most significant being the attempt to visualize the many-electron problem involved in each excitation process and the associated time considerations. The one-electron model is criticized and the conventional X-ray energy level diagram rejected as being incomplete. The theory is fundamental in understanding the present work.

II. The excitation theory according to Parratt

The excitation theory may be presented in connection with the energy level diagram, Fig. 1, proposed by Parratt. In each absorption transition the initial state is a normal, unexcited state, called the ground state. Energy is required in creating any

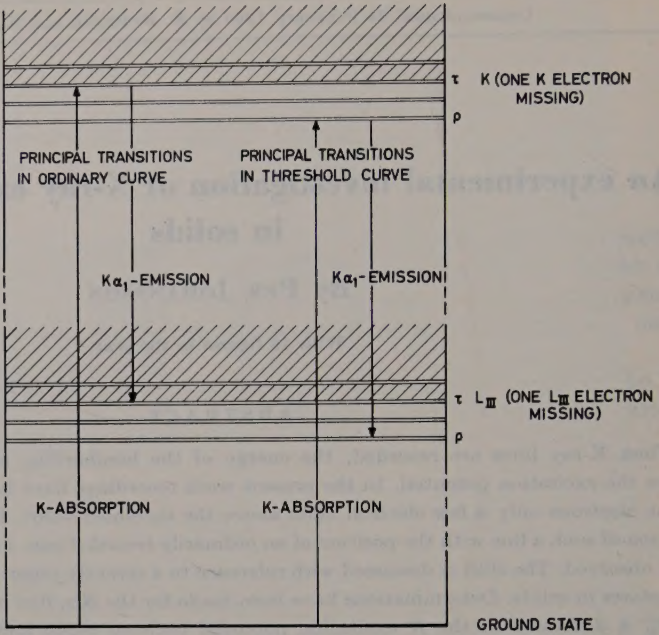
τ K (ONE K ELECTRON MISSING)
p
PRINCIPAL TRANSITIONS IN ORDINARY CURVE
PRINCIPAL TRANSITIONS IN THRESHOLD CURVE
$K\alpha_1$-EMISSION
$K\alpha_1$-EMISSION
τ L_{III} (ONE L_{III} ELECTRON MISSING)
p
K-ABSORPTION
K-ABSORPTION
GROUND STATE

Fig. 1. Energy level diagram according to Parratt. The transition arrows refer to the present work.

other state and consequently all states are reckoned as positive, in relation to this zero reference level, with the K-state at the top. The diagram shown is a one-vacancy diagram; a K-state denotes the energy of the entire system when one electron is missing from the K-shell. (For multiple ionization the energy is altered and a new type of diagram required.) Each type of inner vacancy is represented by a continuum of levels, indicated by the diagonal lines in the figure, and a manifold of discrete excitation states. A theoretical deduction of the density of states due only to the pertinent solid state renders a system of energy bands. The continuum stands for the unoccupied part of this region. The perturbation effects from the inner vacancy are all included in the discrete excitation states. Depending on their origin the latter are of two types. One type, the bound-ejected excitation states, represents the possible energy states of the system in which the ejected electron is still bound in different orbitals to the positive hole it left behind. The states marked τ form the limiting cases, the electron then being at rest at infinity. These ionization τ-states are suggested to be the most significant in conventional X-ray investigations where a large excess of energy is available.

In a many-electron system the total configuration after a collision and the changes in the Coulomb field are essential. Each configuration gives the system a characteristic energy: the valence electrons may be expected in grouping themselves differently, giving a manifold of valence-electron-configuration excitation states, this being the second type of excitation states. Hence, each single state in the conventional diagram is split into a continuum and a set of discrete excitation states. The energy separations of these states will be discussed in greater detail later.

The general theory described has grown out of the need for a more unified interpretation of the details in X-ray spectra. However, the existence of the excitation states as well as their possible importance are up to now far from being confirmed. Applications have been made though, some of which are as follows. In reference [4], Parratt illustrates different features of the theory by known experimental curves. In a recent paper [5], Skolnick and Parratt have attempted to explain phenomena such as line asymmetry and satellites from the general model. Here, then, for the first time the proposal has been worked out in detail, the theoretical treatment giving a semi-quantitative result in accordance with experiment. Some support of the theory is provided by discrepancies reported by Sokolowski [6] and Nordling [7] in comparing their photoelectron data with conventional X-ray absorption results. The energy measured in the two cases may, according to Parratt, be related to the τ-level (Fermi level) of the undisturbed crystal and the lowest bound-ejected excitation state, respectively.

The present work offers quite a new way of testing the validity of the theory. It is an experimental method, proposed by Parratt [4], which approaches the problem in a more direct way than earlier attempts. This method makes a confirmation possible and simultaneously delivers quantitative information about the states concerned.

III. Principles of the present experiment

The experiment suggested employs an apparatus for isochromat measurement with high voltage resolution. With such a spectrometer an intensity curve of a characteristic line is recorded, i.e. with the detector slit set at the peak of the line, we plot the intensity as a function of the anode voltage in the neighbourhood of the voltage threshold, thereby receiving an exact knowledge of the excitation potential.

The actual measurements are arranged as follows: Keeping the voltage fixed at a value above and very near the threshold voltage, we measure the intensity distribution of the line as a function of wavelength by changing the Bragg angle in small steps. According to theory the shape and position of a line so recorded must essentially be determined by the bound-ejected excitation states. Thus, if we record the line at a voltage sufficiently high for producing ionization states in the solid anode, we may expect the line shape to be changed and the peak moved to a slightly different wavelength.

An obvious advantage of the present method in examining the small effects involved should be discussed further. In the common X-ray investigations of absorption edges, a troublesome correction for the spectral window of the instrument has to be applied to the observed curve before interpretation is possible. In the present determination of the wavelength shifts for emission lines this correction can be omitted. The structural details are here revealed simply by comparing two measurements of the same energy spectrum, the recording conditions being identical. By using different accelerating voltages for the impact electrons we are able to change the initial state of the emission process investigated. The measured difference in wavelength is a direct result of the effect to be studied.

IV. The apparatus

The spectrometer is that constructed by Ohlin [8] and the X-ray tube, the one used by Nilsson [9]. Fig. 2 shows the principle. It is a high-vacuum spectrometer employing a bent crystal as monochromator and a Geiger–Müller counter as detector. The high

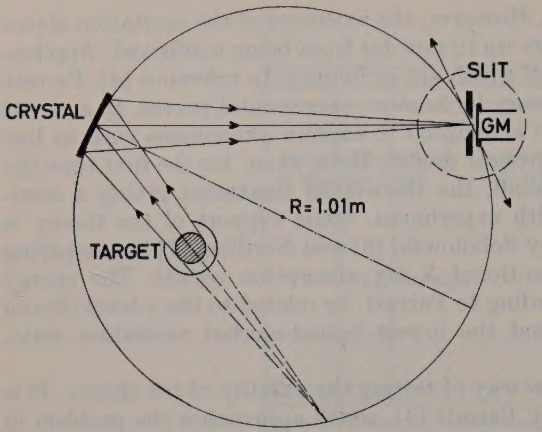

Fig. 2. The principle of the spectrometer.

voltage set is built for precision determinations of isochromats. The possibility of working with a well smoothed and stabilised high voltage—the ripples $\leqslant 1:10^5$—is utilized in the present investigation. The problem of absolute measurement of voltage is here of less interest and is left out of consideration.

A detailed description of the apparatus can be found in reference [9]. Some essential features and changes necessitated by the special requirements of the present work may be mentioned.

The earthed cathode, consisting of a tungsten filament 0.35 mm in diameter, was heated by a current of 10 A. The solid copper target was tightly fastened to the water-cooled anticathode housing. In order to get more effective cooling this was rebuilt to be made up of two concentric copper tubes, the water traversing the interspace (Fig. 3). The crystal used was topaz, surface 101, bent according to Brogren [10] with a radius of 1010 mm. The dispersion was 0.70 mm/X.U. or 0.29 mm/eV in the actual wavelength region. The opening of the crystal holder was widened to 6 × 14 mm giving a higher intensity without any noticeable demunation of the spectral resolution.

Special attention has been paid to the intensity recording device. A commercial GM-tube, Mullard MX-118, was used as detector. This is an argon-filled, halogen quenched counter with a mica end window of 12 μ thickness.

For the determination of the position and intensity distribution of the X-ray lines, the slit with the Geiger counter was moved along the tangent of the Rowland circle (Fig. 2). A ball-bearing arrangement has rendered the motion effectively frictionless. The adjusting micrometer screw has continuously been controlled, the reproducibility being satisfactory.

The spectrometer has earlier been employed in exploring the fine structure at the foot of the excitation curves. A series of similar recordings preceded the present experiment and formed the basis of it. An essential factor in investigations of this kind is the purity of the target. As a matter of fact, no reproducible excitation curves at all could be received if a contamination had entered in the focal spot. Accordingly, in the present work, the isochromats also served as very sensitive contamination detectors.

Great demands are made upon the vacuum properties of the spectrometer. The magnetic lens made a large distance (25 cm) possible between cathode and target,

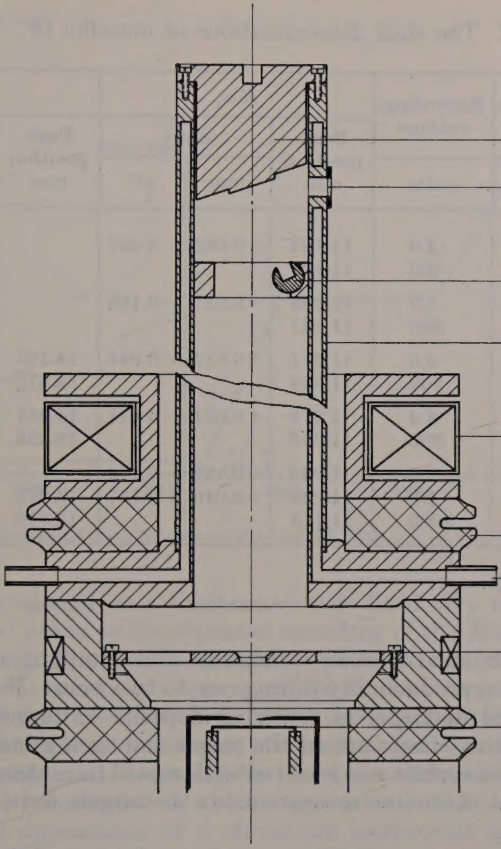

Fig. 3. The inner part of the X-ray tube. *A*, exchangeable copper target; *B*, window with thin Al foil; *C*, evaporation furnace; *D*, anticathode housing, formed by two concentric copper tubes; *E*, focusing magnetic lens; *F*, porcelain insulator; *G*, inlet for cooling water; *H*, copper anode with a 7 mm aperture and an outer ring of evacuation holes; *I*, cathode.

which prevents deposition of tungsten on the latter. The vacuum system consists of two parts, the spectrometer tank and the X-ray tube, separated by a thin aluminium window for the X-rays. The small volume of the X-ray tube was evacuated separately by an efficient high-vacuum pump with a charcoal trap inserted. This arrangement constantly resulted in a final vacuum of 10^{-6} mm Hg, registered during the measurements by an ionization gauge directly attached to the X-ray tube. The target showed no traces of focal spot even after a run of more than ten hours.

V. Measurements and results

A. *Chromium*

For the most part, measurements were carried out for metallic chromium. In the first experiments chromium was evaporated on the copper target using a molybdenum furnace which was mounted in the X-ray tube and heated by the deviated electron

Table 1. The shift determinations of metallic Cr.

No. and type of curve	Slit width along the tangent		Recording voltage	$K\alpha_1$			$K\alpha_2$		
				Peak position	Shift		Peak position	Shift	
	mm	volts	volts	mm	mm	eV	mm	mm	eV
1, T[a]	0.109	0.37	3.0	11.199	+0.002	−0.007			
2, O[a]	0.109	0.37	500	11.197					
3, T	0.242	0.82	1.0	11.298	+0.031	−0.105			
4, O	0.242	0.82	500	11.267					
5, T	0.356	1.2	0.5	11.371	+0.012	−0.041	14.185	+0.113	−0.384
6, O	0.356	1.2	500	11.359			14.072		
7, T	0.356	1.2	3.0	11.376	+0.021	−0.071	14.081	−0.015	+0.051
8, O	0.356	1.2	500	11.355			14.096		
9, T	0.118	0.40	1.5	11.260	+0.082	−0.279			
10, T	0.118	0.40	2.0	11.224	+0.046	−0.157	13.975	+0.065	−0.221
11, O	0.118	0.40	3000	11.178			13.910		

[a] T = Threshold; O = Ordinary.

beam (see Fig. 3). With ideal furnace conditions the sampling chromium layer always gave satisfactory reproducibility during one to two hours. For our purpose a longer time was required and several renewing deposits of target material were necessary. By electroplating chromium on the target and then grinding the surface, however, one very resistive surface was received with regard to contamination (mainly oxidation). In the present chromium measurements the targets were prepared in this manner.

For every isochromat to be recorded an exact determination of the position of the X-ray line must be made. In order to plot the X-ray line the narrowest possible slit width is commonly employed, the slit-width then being widened for intensity reasons when the corresponding isochromat is recorded. In the present investigation such a method could not be adopted, as any touch of the slit would disrupt the critical shift determination. Hence the same slit-width had to be used in each of the three recordings necessary for a shift determination. The choice of the slit-width is essentially determined by the time accessible for measurement and also by the unfavourable signal-to-noise ratio of the threshold curves. Consequently, a wide slit had to be chosen. Four different slit-widths have been used, varying between 0.37 eV and 1.2 eV (see Table 1), corresponding to 15 and 50 % of the half widths, respectively. In accordance with theory, the line width is influenced very little by these changes. The observed values of the full width of $K\alpha_1$ at half maximum intensity, ordinary curve (see below), varied between 2.30 and 2.38 eV. The small deviation from the value 2.31 eV obtained by Parratt [11] with a two-crystal spectrometer (observed, uncorrected value) indicates that the crystal employed in the present work was of a reasonably good quality.

Each shift determination consists of three curves, recorded consecutively with the same target plate: (1) isochromat, (2) threshold curve, and (3) ordinary curve. The term "threshold curve" refers to the recording of the intensity of the X-ray line as

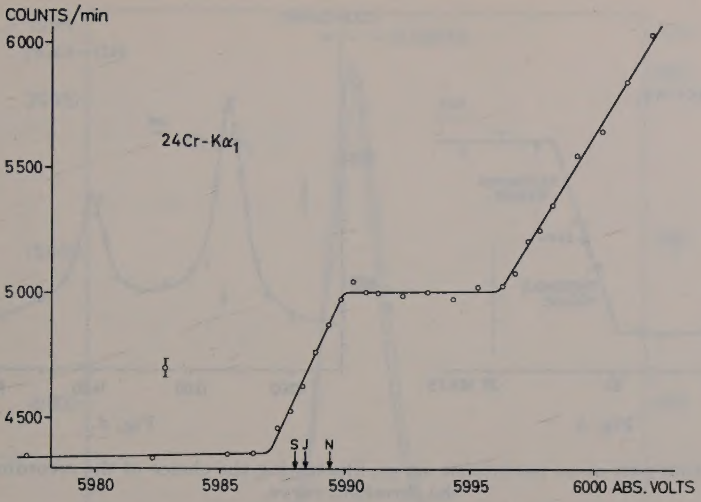

Fig. 4. Isochromat of metallic Cr in the neighbourhood of the K-excitation potential.

a function of wavelength at a constant voltage fixed very near the threshold value. "Ordinary curve" refers to the repeated recording of the X-ray line with the voltage kept constant and high above the excitation potential. Starting with a new target the sequence of the measurements was specified in order to guarantee reproducibility. The recording of the threshold curve, the most important determination, had to be done as early as possible after insertion of a fresh target to avoid contamination effects. The preceding isochromat, necessary for the choice of recording voltage for the threshold curve, could be recorded in a short time (about 20 min.).

The general appearance of a chromium isochromat is shown in Fig. 4. The continuous radiation forms a background of almost constant intensity. When the excitation potential is reached, the emission of the characteristic radiation is indicated by a sudden intensity rise. A fine structure appears. After the first slope, the "edge", a constant region follows, the "plateau", ended by the second intensity rise. The edge is about 3 eV wide, the plateau 6 eV wide. The reproducible height of the plateau is important in the present investigation, as all the threshold curves have been recorded in this region. The maximum value of the line intensity, the height of the plateau, was about 20 % of the background, varying slightly with slit-width and target.

The recording voltage of the threshold curves is calculated from a voltage value corresponding to the centre of the edge, here called the threshold voltage.[1] An example is shown in Fig. 5. The recording voltages have been varied between 0.5 and 3.0 volts above the threshold voltage (Table 1).

A recording of a threshold curve is given in Fig. 6. The intensity is plotted against the scale of the micrometer screw. The total number of registered points as well as the number of counts, and hence the statistical resolution for each point, are limited

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[1] The choice of reference point is of secondary importance in the present relative measurements, while it forms the central problem in absolute measurements. If we accept the commonly used inflexion point theory, the arrows in Fig. 4 indicate the values of the K-excitation potential according to Sanner [12], Nilsson [9] and the author (present value), being respectively 5988.0, 5989.4 and 5988.4 V.

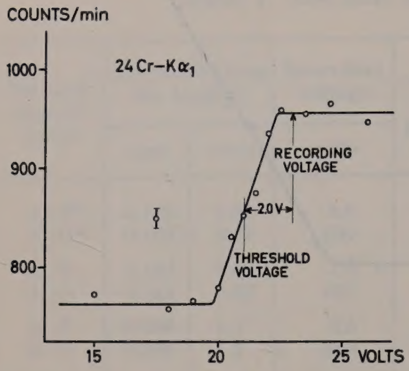

Fig. 5.

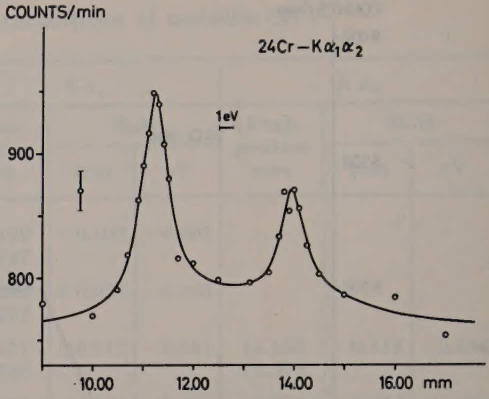

Fig. 6.

Fig. 5. The actual part of an isochromat curve, illustrating the choice of the recording voltage of the threshold curve.

Fig. 6. Threshold curve of Cr. The recording voltage only 2.0 volts above the threshold. Compare Fig. 5.

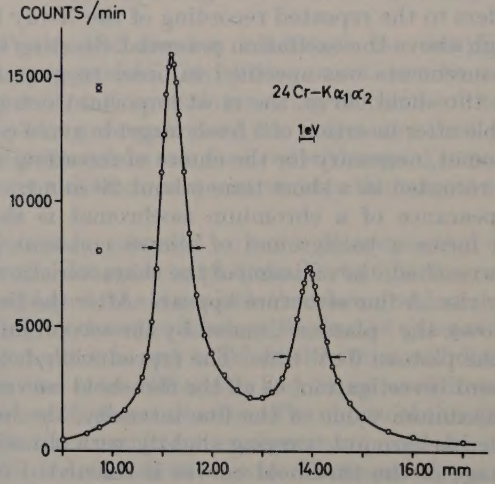

Fig. 7. Ordinary curve of Cr. The recording voltage 500 volts above the threshold.

by the time available for recording, being at the highest about 4 hours. The emission current used was 20 mA. In spite of the low intensity (compare Fig. 5) pronounced lines are obtained.

Fig. 7 shows the corresponding recording with a high over-voltage—an ordinary curve. In order to increase the accuracy of the position these lines were recorded twice, first from the short and then from the long wavelength side. The recording voltages used, 500 and 3000 volts above the threshold point, have been kept fixed and ripple-free with the same accuracy as for the threshold lines. Owing to the in-

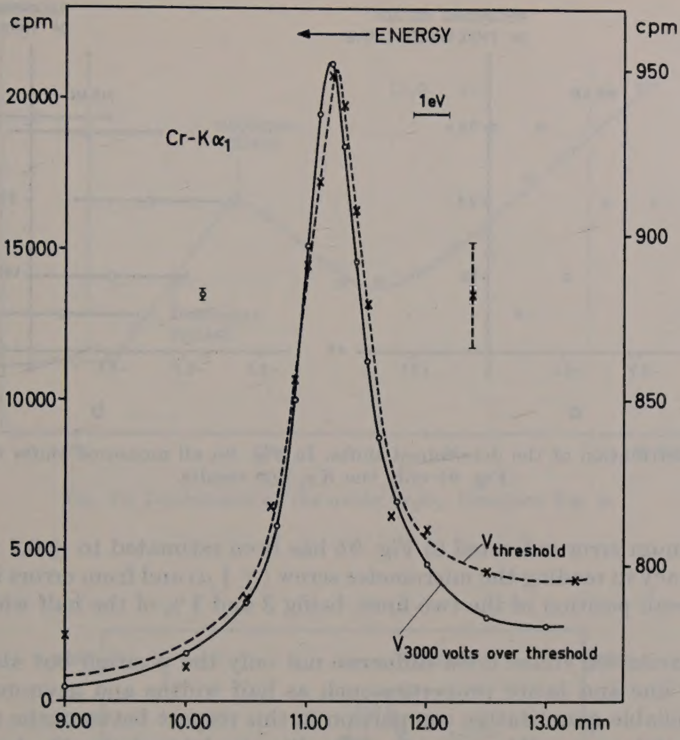

Fig. 8. Threshold curve and ordinary curve for direct comparison.

tensity rise with the exciting voltage the emission had to be lowered to about 5 mA. The two types of emission curves consecutively recorded are drawn in Fig. 8, making a comparison possible.

The plottings in the figures are given in their originally observed form corrected for the dead time of the counter. All the calculations also relate to this kind of curves.

A survey of the shift determinations for chromium is given in Table 1. The peak position value represents the intersection between the curve and the diameter of horizontal chords. The shift refers to the peak position of the threshold line in relation to that of the ordinary line. A displacement to the right in the figures means a negative shift with respect to energy. The first two shift determinations, curves No. 1 through 4, were made for the $K\alpha_1$ line only. (The recording of the threshold curve, No. 9, could not be fully completed owing to intensity instabilities, and hence the shift given has less accuracy.)

Fig. 9 gives a diagrammatical survey of the results. The horizontal axis indicates the obtained shifts in eV. In order to reveal any trend in the shift owing to a different selection of recording voltage at the threshold curves, this voltage is plotted along the vertical axis. In Fig. 9*a* all the values are inserted, the mean value being -0.13 eV. By intensity reasons the determinations of $K\alpha_2$ are not as reliable as those of $K\alpha_1$, which is also seen from the larger distribution. The $K\alpha_2$ values together with the shift from curve No. 9 have been excluded in Fig. 9*b*, resulting in a mean value of -0.08 eV.

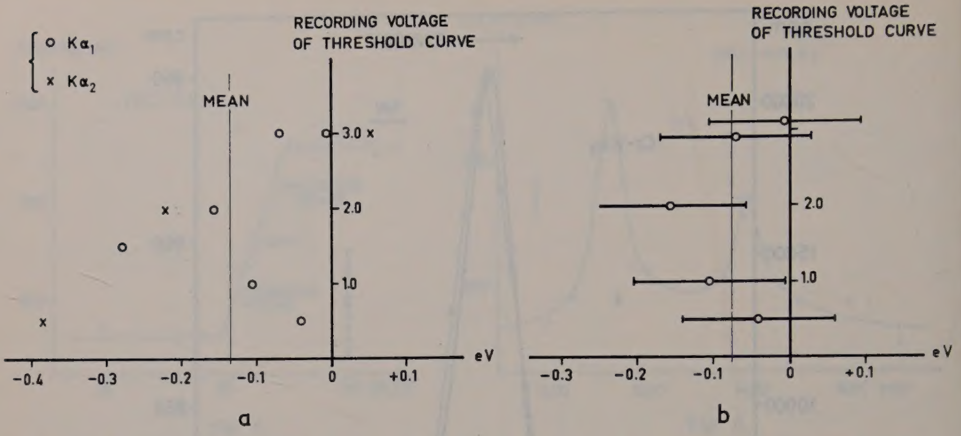

Fig. 9. The distribution of the determined shifts. In Fig. 9*a* all measured shifts are plotted, in Fig. 9*b* only the $K\alpha_1$-line results.

The maximum error indicated in Fig. 9*b* has been estimated to ± 0.1 eV. It arises from inaccuracy in reading the micrometer screw ($\pm 1\ \mu$) and from errors in identification of the peak position of the two lines, being 3 and 1 % of the half widths, respectively.

Possible excitation states must influence not only the position but also the shape of an X-ray line and hence properties such as half widths and asymmetries are of interest. A reliable quantitative comparison in this respect between the two types of curves has not been possible owing to difficulties in determining the background of the threshold curves. Qualitatively the half width remains unchanged. As seen from Fig. 8, the threshold line, however, is more symmetric than the ordinary one, the latter having an asymmetry of 1.27 (mean value).

B. *Chromium oxide Cr_2O_3*

Some preliminary results may be presented for the semiconductor Cr_2O_3. Great attention has been paid to getting a reliable oxide layer on the target. The method of preparation was according to reference [13]. A solid copper target, chromiumplated as before, was heated in air to 600°C. The oxide film formed in this way consists entirely of Cr_2O_3. The thickness of the film depends on the oxidation time and could be determined roughly from the interference colours [13], and more exactly by coulometric reduction [14]. Oxidations of 50 and 90 minutes gave thicknesses of 600 Å (blue surface) and 900 Å (green-gray surface), respectively.

The targets prepared in this manner have given high reproducibility of the experimental results. The isochromats of the oxide (Fig. 10) differ in an essential way from those of the metal. The plateau is here replaced by a pronounce intensity minimum. The width of the edge is 4 to 5 volts. Owing to a lower signal-to-noise ratio (12 %) and the limited recording time the slit width had to be widened to 2.3 eV, giving a half width value of (3.65 ± 0.05) eV for the ordinary $K\alpha_1$ line. Three $K\alpha_1$ shift determinations have been made. The recording voltages of the threshold curves have been 2 volts in two cases, and 25 volts in the other.

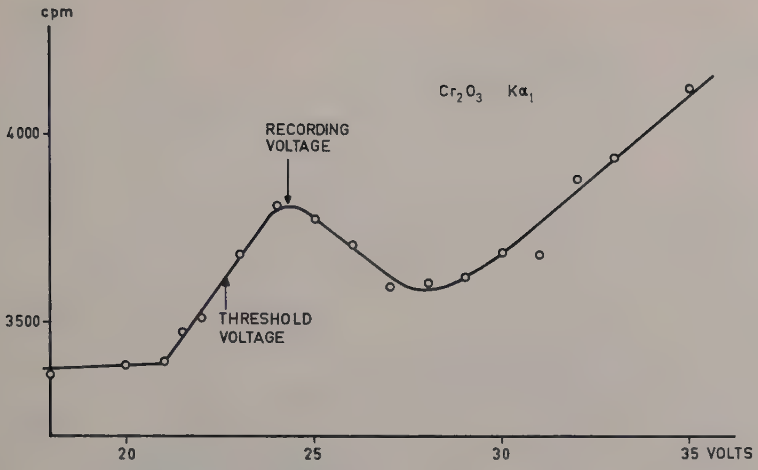

Fig. 10. Isochromat of the oxide Cr_2O_3. Compare Fig. 4.

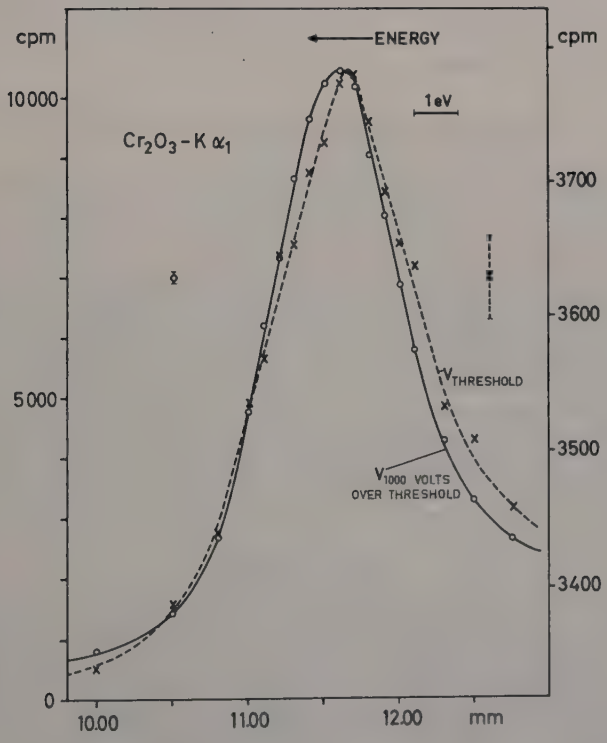

Fig. 11. Threshold curve and ordinary curve of Cr_2O_3.

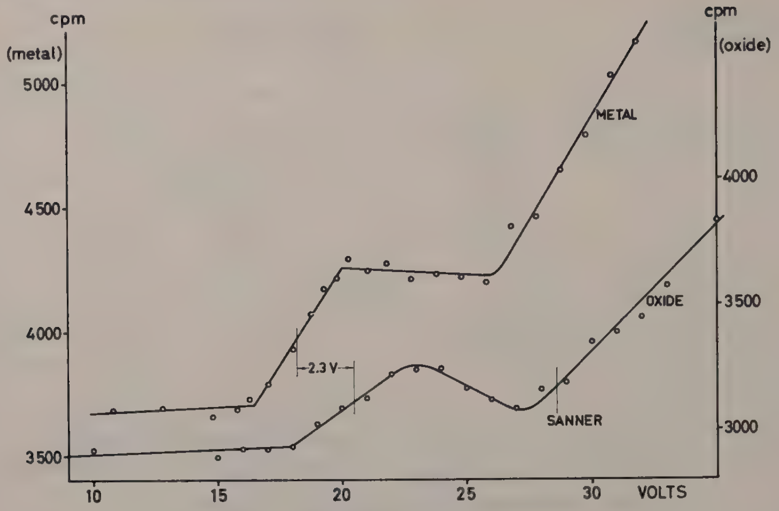

Fig. 12. Isochromats of Cr and Cr_2O_3.

The result indicates a shift in the same direction as for metallic chromium. The shift of the oxide is greater, being − 0.37 and − 0.29 eV in the 2-volt recordings. One of these determinations is shown in Fig. 11. For the 25-volt recording no measurable displacement could be observed.

C. *Chemical shift measurements of Cr—Cr_2O_3*

As seen from the discussion below an observable chemical shift between metal and oxide is of interest for the excitation theory. Attempts to determine this shift were made by two methods: (1) by absolute measurements of the excitation potential of chromium and chromium oxide, and (2) by recording consecutively isochromats for the oxide and the metal. The latter and more reliable method could be realized by the evaporation furnace inserted in the X-ray tube. A measurement according to the relative method is illustrated in Fig. 12. As shown in the figure, the oxide requires a higher excitation energy than the metal. The size of the shift amounts to 2.4 eV. The value is an average of 7 runs, the greatest deviation from the mean value being 0.4 eV. At absorption measurements by the photographic method Sanner [12] has found a shift of 10.4 eV. The discrepancy arises by the fact that Sanner has not taken into account the weak foot structure of the oxide curve, as seen from Fig. 12.

VI. Discussion

When analyzing the present results it is important to realize the magnitude of the observed effect. The experimentally measured energy shift is small for metallic chromium—absolutely the shift is 0.1 eV and relatively 2×10^{-5}—and of the same order of size as the calculated accuracy. But even so the effect might be regarded as fully established for metal as well as for oxide. The result of the test can be summarized in three points:

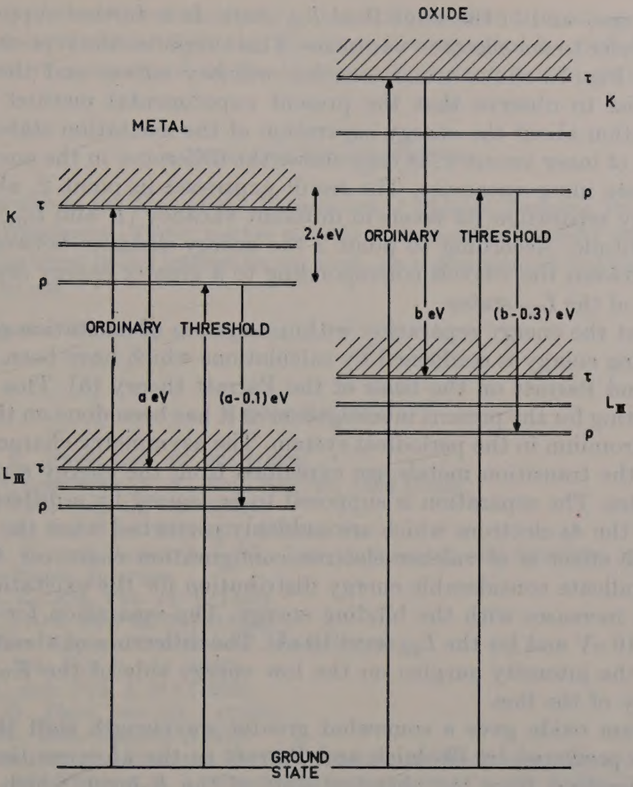

Fig. 13. Schematic diagram of the proposed transitions and the interpretation of received shifts in metal and oxide.

1. The position in the spectrum of an X-ray line is dependent upon the voltage for excitation energies slightly above the threshold value.
2. The energy shift between threshold curves and ordinary curves is small.
3. The emission energy is lower for the threshold line than for the ordinary line.

The measurements no doubt give a support to Parratt's theory (chap. II). In order to illustrate the interpretation of the present result we use a model of the energy level diagram, according to Parratt, Fig. 13. It is here supposed that the excitation states, mainly of bound-ejected type, which characterize the threshold curves have a lower energy than the ionization states. We further assume that an emission transition takes place between similar states—τ to τ, ϱ to ϱ etc.—corresponding to an unchanged electron configuration during the emission process itself. Such an assumption is based theoretically on time considerations: the electron jump is supposed to take place in less than 10^{-18} sec while the time of regrouping of the valence electrons is determined by the mean life of an inner vacancy $\approx 10^{-16}$ sec. That a transition occurs between similar states only is supported experimentally by the fact that no tendency to voltage dependence appears in the shifts in Fig. 9*b*. Such a tendency might be expected if the threshold transition could originate in different initial *K*-states, determined by the recording voltage, and in the same final L_{III} state. It is further supposed that both types of lines refer to one-electron vacancies. This simplifies the representation to one diagram only. Fig. 13 shows transitions for ordinary curves and threshold curves.

It is essential to observe that the present experimental method does not give direct information about the energy separation of the excitation states belonging to the same type of inner vacancy. It only shows the difference in the energy separation for two separate inner vacancies. The result expressed in point 2, above, indicates that the energy separation for levels in different vacancy (K and L_{III}) is of a similar order of magnitude. According to point 3 the energy distance between the ϱ-levels is less than between the τ-levels corresponding to a greater energy separation of the K-states than of the L_{III} states.

The fact that the energy separation within a system of excitation states increases with the binding energy is confirmed by calculations which have been made recently by Skolnick and Parratt on the basis of the Parratt theory [5]. This work is particularly interesting for the present investigation as it has been done on the metal 25 Mn adjacent to chromium in the periodical system. The asymmetry characteristics of the K-doublet of the transition metals are explained from the energy separation of the excitation states. The separation is supposed to be caused by a difference in the arrangement of the 4*s* electrons which are suddenly perturbed when the inner vacancy is created. The effect is of valence-electron-configuration character. Quantitatively their results indicate considerable energy distribution for the excitation states. This energy spread increases with the binding energy. The separation for the K-level of manganese is 16 eV and for the L_{III} level 10 eV. The difference of about 6 eV explains satisfactorily the intensity surplus on the low energy side of the $K\alpha_1$ line, causing the asymmetry of the line.

The chromium oxide gave a somewhat greater wavelength shift than the metal. This has been predicted by Skolnick and Parratt in the aforementioned paper [5]. It can be understood from the chemical shift of the K-level, which is determined in a separate investigation (chap. V, C). The K-excitation potential turned out to be 2.4 V greater for the oxide than for the metal. We suppose that the absorption transitions go to the ϱ-states (see Fig. 13). It is natural to assume that the chemical shift decreases with binding energy ($b > a$). As the energy separation within the different vacancy types increases with the binding energy, one can expect a greater wavelength shift between the ordinary curve and the threshold curve of the oxide than between those of the metal.

The present experimental method does not give direct information about the size of the energy separation within the same type of states. However, it could be possible to make an estimation of the size from the present result. In the absorption process during isochromat recordings the transitions probably go to the excitation states of the lowest energy.[1] The ordinary curve on the other hand is supposed to be caused by a transition between the highest states. Hence, the energy shift found reproduces the difference between the *total* energy separation in two types of states. For chromium the binding energy is altered with a factor 10 in going from the K-level (5990 eV) to the L_{III} level (570 eV). The energy spread, which increases with energy, is supposed to change approximately at the same rate. The corresponding shift is measured to 0.1 eV. This can be understood only if the total energy separation for each type of inner vacancy is of the same magnitude as the shift itself or at most one electron volt. This value is in accordance with the discrepancies reported by Sokolowski [6] and Nordling [7] but it is one-tenth of the theoretically calculated separations [5].

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[1] In this way the fine structure preceding the edge, particularly in Ti as found by Nilsson [9], gets an interesting interpretation.

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